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Synthetic & Structural Studies on the Polymeric Complexes of Terephthaloyl-bis-(N-phenylhydroxamic Acid) (TPHA) & Sebacyl-bis-(N-phenylhydroxamic Acid) (SPHA) with Co(II), Ni(II), Cu(II) & Zn(II)

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Polymeric complexes of terephthaloyl-bis-(N-phenylhydroxamic acid) (TPHA) and sebacyl-bis-(N-phenylhydroxamic acid) (SPHA) with Co(II), Ni(II), Cu(II) and Zn(II) have been prepared by the reaction of the corresponding ligands with transition metal ions in dimethylformamide medium. Polymers formed have been characterised by their elemental analysis. Thermal stabilities of the polymers have been investigated by carrying out differential thermal analysis and thermogravimetric analysis. The structures of the polymeric complexes are assigned on the basis of their reflectance and infrared spectral and magnetic susceptibility data.

Hydroxamic acids are an important class of reagents and form complexes with various metal ions[1-4]. In the present paper, preparation of terephthaloyl-bis-(N-phenylhydroxamic acid) (TPHA) and sebacyl-bis-(N-phenylhydroxamic acid) (SPHA) and their polymeric complexes with Co(II), Ni(II), Cu(II) and Zn(II) have been reported for the first time. Besides the synthesis and examination of their thermal stability, present work describes structural characterisation of these polymeric complexes on the basis of elemental analysis, infrared and reflectance spectra and magnetic susceptibility measurements.

Materials and Methods

All the chemicals used as starting materials in the synthesis of ligands and coordination polymers were of chemically pure quality. If required, these were further purified by standard procedures.

Preparation of ligands

Terephthaloyl-bis-(N-phenylhydroxamic acid) (TPHA) and sebacyl-bis-(N-phenylhydroxamic acid) (SPHA) were prepared by the modified method of Priyadarshini and Tandon[5] based on the Schotten-Baumann reaction. N-Phenylhydroxylamine (0.25 *M*), ethanol (50 ml), sodium bicarbonate (0.5 *M*) and distilled water (25 ml) were taken in a 250 ml beaker. To this, acid dichloride (0.1 *M*) dissolved in diethyl ether (100 ml) was added over a period of 45 min with constant stirring. A granular solid separated which was filtered and triturated with saturated solution of sodium bicarbonate to remove any acidic impurities. The products were obtained in low yields (60 to 70%) and were crystallized with difficulty from dimethylformamide (DMF) (m.p. SPHA 152° and TPHA 232°). TPHA melted with decomposition. TPHA [Found: C, 68.55; H, 4.81; N, 7.80; Calc. for $C_{20}H_{16}O_4N_2$: C, 68.96; H, 4.80; N, 7.81%]. SPHA [Found: C, 67.60; H, 7.39; N, 7.30; Calc. for $C_{22}H_{28}O_4N_2$: C, 68.76; H, 7.29; N, 7.29%].

Preparation of polymers

The ligand (0.01 *M*), metal acetate (0.01 *M*), and DMF (50 ml) were heated on a waterbath for 2 hr. The insoluble polymers formed were filtered and throughly washed several times with dimethylformamide and ethanol till free from unreacted reactants.

The polymers were obtained as amorphous powders and were found to be insoluble in almost all the common organic solvents. The elemental analyses and proposed compositions for these polymers are given in Table 1.

Carbon, hydrogen and nitrogen were estimated usuing a Coleman's analyser.

IR spectra were recorded on a specord IR-75 instrument in the range 4000-400 cm^{-1} using nujol mull.

A single beam Carl-Zeiss USU-2-p-spectrophotometer was used for recording reflectance spectra of polymers and magnesium carbonate was used as a reference sample. A DTA apparatus fabricated at IIT, Bombay was used for recording differential thermograms of the polymers. The heating rate was maintained at 7°/min. A Stanton-Redcroft thermogravimetric balance with an automatic recorder (BARC, India) was used for thermogravimetric analysis. The analysis was carried out in air with 100 mg of a sample taken in a platinum crucible. The

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Table 1—Elemental Analyses and Decomposition Temperatures of Ligands and Polymers

Proposed composition (Dec. Temp., °C)	Found (Calc.), %				Colour	$\mu_{eff.}$ (B.M.)
	C	H	N	M		
$[Co(a)]_n$	58.65	3.56	6.78	14.40	Brown	3.91
(290)	(58.98)	(3.44)	(6.88)	(14.48)		
$[Ni(a)(H_2O)_2]_n$	55.00	4.16	6.55	13.23	Yellow	3.44
(300)	(54.21)	(4.01)	(6.32)	(13.26)		
$[Cu(a)]_n$	57.20	3.64	6.88	14.88	Yellowish	1.88
(260)	(58.32)	(3.40)	(6.80)	(15.43)	green	
$[Zn(a)]_n$	58.10	3.22	6.82	15.62	White	—
(270)	(58.06)	(3.39)	(6.77)	(15.82)		
$[Co(b)]_n$	58.75	5.71	6.20	14.45	Light pink	4.67
(355)	(58.61)	(5.87)	(6.32)	(13.30)		
$[Ni(b)(H_2O)_2]_n$	56.65	5.74	6.76	12.24	Light green	3.39
(320)	(56.15)	(5.85)	(6.27)	(12.26)		
$[Cu(b)]_n$	58.80	6.10	6.22	13.88	Dirty green	1.83
(375)	(58.99)	(5.81)	(6.26)	(14.19)		
$[Zn(b)]_n$	58.50	5.99	6.23	14.39	White	—
(330)	(58.74)	(5.79)	(6.23)	(14.55)		

(a = TPHA, b = SPHA)

heating rate was maintained at 3°C/min. Magnetic susceptibilities of polymers were determined by Gouy's method.

Results and Discussion

An IR band around 2800 cm^{-1} has been assigned to O – H stretching vibration in this type of hydroxamic acids[6]. In the present case this band appears at 3170 cm^{-1} in SPHA and TPHA ligands. Bands appearing at 1615 and 1595 cm^{-1} in SPHA may be due to the resonating structures of N – N-(– C = O)-OH moiety. In the case of TPHA it appears at 1600 cm^{-1}. An intense band appearing at 3275 cm^{-1} is due to free N – H stretching whereas the band appearing at 895 in SPHA and 890 cm^{-1} in TPHA is assigned to N – O stretching vibration.

The hydroxamic acids generally form five membered chelates with metal ions coordinating through >N – O and > C = O oxygens.

As is anticipated, the band due to O – H group disappears in polymers. The band due to carbonyl group is shifted towards lower frequency side indicating the formation of C = O → M coordinate bond. The N – O band in polymer is found to have been shifted slightly to higher frequency side with increase in its intensity. Medium bands appearing in the region of 520 to 565 cm^{-1} are assigned to M – O bonding in polymers[7].

Reflectance spectra and magnetic properties

A band appearing around 18.69 kK in Co(II)-TPHA and around 18.60 kK in Co(II)-SPHA polymers may be assigned to $^4A_2 \rightarrow {}^4T_1(P)$ transition in tetrahedral field[8].

Magnetic data of Co(II)-TPHA and -SPHA polymers also support the tetrahedral geometry of these complexes. A band appearing at 25.64 kK in Ni(II)-SPHA and at 28.00 kK in Ni(II)-TPHA polymer is due to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition. The magnetic moment value also confirms the octahedral geometry of the complexes.

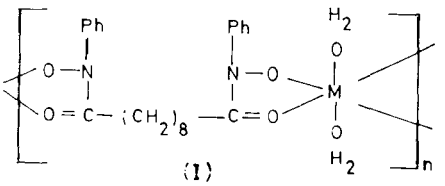
Broad bands around 15.38 kK and 12.66 kK in Cu(II) polymers of SPHA occur due to $d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions respectively[9].

In TPHA-Cu(II) polymer, however, only one band is observed around 15.88 kK which may be due to $d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$ transition. Thus, in both the cases, the square planar geometry is predicted[10].

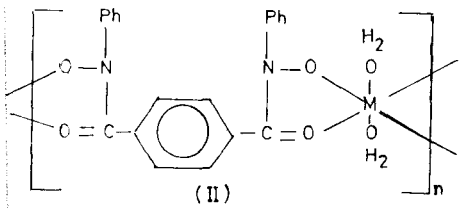
Thermal studies of polymers

Co(II) and Cu(II) complexes of TPHA show a large exotherm in the range 310-400°C (390-520°C for SPHA complexes) while the range for Ni(II), Zn(II) complex is 310°-340°C (360°-500°C for SPHA complexes). In addition to this, Co(II) and Cu(II) complexes of TPHA show a sharp exotherm at ~230°C (250°C for SPHA complexes) while for Ni(II) complex it occurs at ~300°C (310°C for SPHA complex). Zn(II)-TPHA complex shows no such sharp exotherm.

It has been observed in the case of Co(II) and Cu(II) polymers that this sharp exotherm is not associated with mass loss in TGA. In Ni(II) polymer



(I)



(II)

this exotherm is almost merged with the large exotherm.

Decomposition temperature of the polymers are given in Table 1.

On the basis of above studies, structures (I) and (II) are proposed for Ni-SPHA and Ni-TPHA polymers respectively. In case of Co(II), Cu(II) and Zn(II) complexes of SPHA and TPHA water of coordination is absent.

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